Indian J. Phys. **73A** (3), 323–328 (1999)

IJP A
— an international journal

Optical properties of lead-bismuth glasses

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Received 4 June 1998, accepted 3 November 1998

Abstract : The optical transmission and absorption spectra in (UV-VIS) have been recorded in the wavelength range 350–800 nm for different compositions of lead-bismuth-glasses. The various optical properties such as absorption coefficient (α), optical energy gap (E_{opt}), refractive index (n_0), optical dielectric constant at infinite high frequency (ε'_∞), measure of extent of band tailing (ΔE), const B and ratio of carrier concentration to the effective mass (N/m^*) have been evaluated. The effect of composition of glasses on these parameters have been discussed. It has been indicated that a small modification of the glass composition can lead to an important change in all the optical properties. These results are interesting, showing nonlinear behaviour for all the parameters being investigated. The optical parameters, are found to be almost the same for different glasses in the same family.

Keywords : Optical properties, lead-bismuth glasses, non-linear behaviour

PACS Nos. : 61.43.Fs, 78.20.Ci

1. Introduction

Charge transport measurements in disordered semiconductors have been of considerable interest recently, because they can provide information about the electronic structure of the materials [1,2]. The study of the electrical, optical and structural properties of glassy semiconductors has increased considerably [3].

The non-linear optical properties of B_2O_3-based glasses have been reported by Terashima *et al* [4]. The effects of iron on the optical, physical and structure properties of several iron phosphate and sodium-iron phosphate glasses were investigated using X-ray photoelectron spectroscopy (xps), Mossbauer spectroscopy and IR by Wang *et al* [5].

The nature of the optical energy gap of rare earth doped glasses was studied and the effect of composition on the position of the absorption edge and the value of the so called optical energy gap was investigated by Sharma *et al* [6].

The optical parameter like refractive index is an important parameter for the design of optical components such as prism, windows and optical fibres [7]. Optical properties and chemical durability of lead-indium-aluminium phosphate glasses prepared by a wet-chemical process have been investigated by Guo *et al* [8] The frequency dependent dielectric and optical properties of binary semiconducting glasses in the system V_2O_5-TeO_2PbO have been measured as a function of lead-content and the effect of composition on refractive index, dielectric constant and optical phonon frequency have been discussed by Memon *et al* [9]. The work on optical and electro-optical properties of Ga_2O_3-PbO-Bi_2O_3 and nonlinear optics was reported by Marta *et al* [10]. Burghate *et al* [11] have reported optical properties of lead-bismuth titanate glasses. The effect of composition of glasses on this optical parameters have been discussed. Linear and nonlinear optical properties of chalcogenide glass were investigated by Hajto *et al* [12]. Optical properties of semiconducting bismuth glasses were reported earlier [13]. Very little work has been done on the optical properties of lead-bismuth oxide-glasses. Therefore it has been decided to study the optical parameters of lead-bismuth oxide-glasses. The intention to study the optical properties of these glasses by UV-VIS spectra is to investigate the existence of localized states near band edge.

2. Experimental details

2.1. *Preparation of samples :*

Glass sample under investigation were prepared in the laboratory by mixing appropriate amount of Bi_2O_3 and PbO (mol %) using Anala-R grade chemicals. A homogeneous

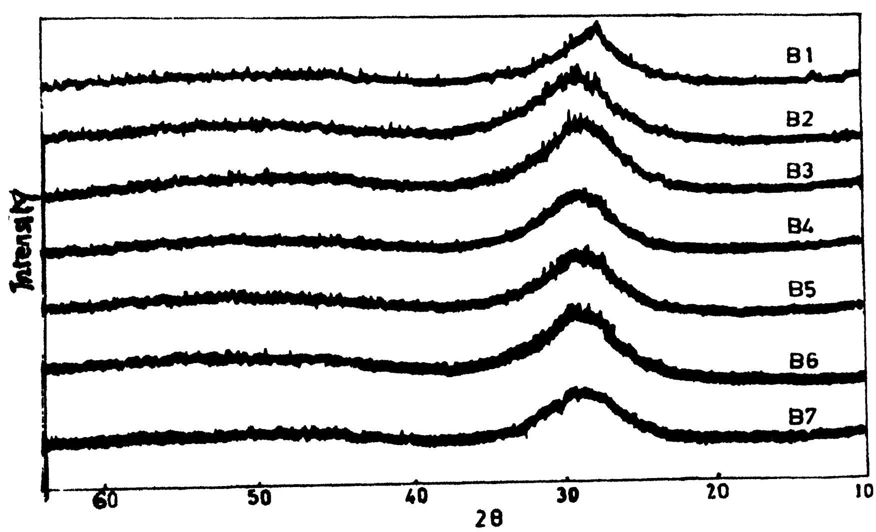

Figure 1. XRD patterns of intensity *vs* 2θ curves of glass samples.

mixture of two powders was prepared and fired in a fireclay crucible at 1000 ± 10°C for half an hour in an automatically temperature controlled muffle furnace. The glass samples were then formed by quenching the melt on a steel plate held at room temperature. The X-ray diffractograms of all the glass samples are shown in Figure 1. The absence of peak in the X-ray spectra, confirmed the amorphous nature of glass samples.

The absorbance A and transmittance t of glass samples were measured by means of CARY 2390 double beam automatic scanning spectrophotometer (at Regional Sophisticated Instrumentation Centre, Madras) in the spectral range 350–800 nm at normal incidence. The spectral dependence of both A and t on composition of the glasses is shown in Figure 1.

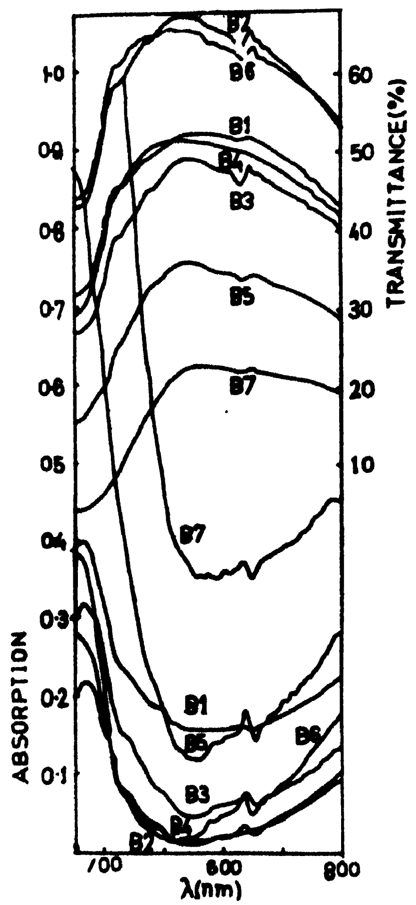

Figure 2. Spectral dependence of both absorption and transmittance *versus* (λ).

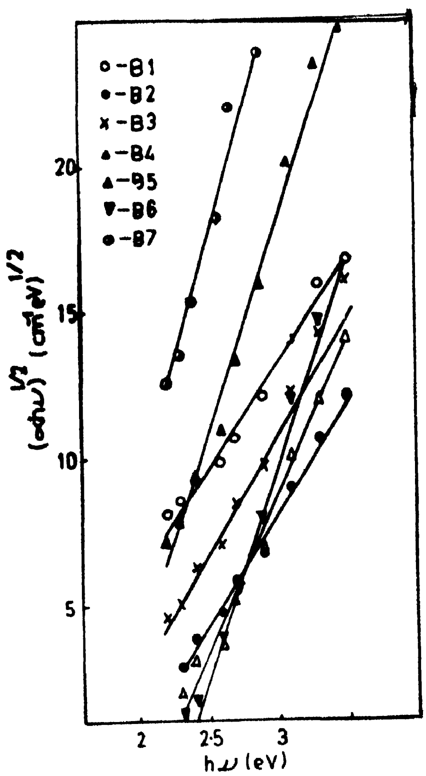

Figure 3. $(\alpha h\nu)^{\frac{1}{2}}$ *versus* $h\nu$ of glass samples.

2.2. Theory :

The optical absorption coefficient, $\alpha(v)$ at a given frequency (v) is given by [14],

$$\alpha(v) = \frac{4\pi\sigma_{\min}}{Cn_0\Delta E}\cdot\frac{(hv - E_{\text{opt}})^r}{hv}, \tag{1}$$

where $\sigma_{\min}$ is the extrapolated dc-conductivity at $T = \infty$, n_0 is the refractive index, C is the velocity of light, ΔE is a measure of the extent of band tailing, hv is the photon energy, E_{opt} is the optical energy gap, $r = 2$ is a number which characterizes the transition process, and

$$B = \frac{4\pi\sigma_{\min}}{Cn_0\Delta E} \quad \text{is the constant.}$$

The reflectance was calculated using the equation

$$t = (1 - R)^2 \exp(-A). \tag{2}$$

The relation between optical dielectric constant ε' and the square of wavelength λ^2 is given by

$$\varepsilon^1 = n^2 = \left(\frac{1+\sqrt{R}}{1-\sqrt{R}}\right)^2 = \varepsilon^1_\infty - \frac{e^2}{\pi C^2}\cdot\frac{N}{m^*}\lambda^2, \tag{3}$$

where ε^1_∞ is the dielectric constant at infinite high frequency, e is the electronic charge and N/m^* is the ratio of carrier concentration to the effective mass.

3. Results and discussion

Figure 3 show the plots of $(\alpha hv)^{1/2}$ *versus* hv for different compositions of glass samples. The most satisfactory representation is obtained by plotting the quantity $(\alpha hv)^{1/2}$ as a function of hv. Similar behaviour was also observed by other workers [15]. The observed behaviour suggests forbidden indirect transition for some glassy and amorphous material. The values of optical energy gap E_{opt} obtained from the extrapolation of the linear region and constant B from the slopes of the derived curves are shown in Table 1. The extrapolated

Table 1. Variation of optical energy gap (E_{opt}), dielectric constant at infinite high frequency (ε^1_∞), refractive index (n_0), constant (B), measure of the extent of band tailing (ΔE) and the ratio of carrier concentration to the effective mass (N/m^*) with different glass composition.

Sample No.	Glass composition (mol %)		Optical gap (E_{opt}) eV	Measure of extent of band tailing (ΔE) eV	Dielectric constant at infinite frequency (ε^1_∞)	Refractive index (n_0)	Constant B ($\text{cm}^{-1} \times \text{eV}^{-1/2}$)	Ratio of carrier concentration to the effective mass ($N/m^* \times 10^{21}\text{cm}^{-3}$)
	Bi_2O_3	PbO						
B1	80	20	1.34	4.460	10.2	2.86	52.89	1.83
B2	70	30	2.08	1.600	9.0	2.72	56.25	0.80
B3	60	10	1.82	0.470	15.0	3.49	69.44	1.22
B4	50	50	2.30	0.230	12.6	3.47	119.00	1.22
B5	40	60	1.84	0.099	17.7	4.08	204.08	0.61
B6	30	70	2.40	0.099	6.6	2.48	159.55	0.30
B7	20	80	1.55	0.016	23.7	4.85	277.77	0.61

de-conductivity (Burghate [16]), σ_{min} at $t = \infty$ is obtained from the plot of log σ *versus* $1/T$ (plot not shown). The values obtained for E_{opt} for the seven different compositions of glass samples are found to be non linear. Similar fact is observed in As–S, Ge–Se, As–Se and Ag–As systems investigated by Hajto *et al* [12].

The dielectric constant ε^1 *versus* λ^2 plots shown in Figure 4 are linear, verifying eq. (3). Values of ε_∞^1 and N/m^* determined from the extrapolation of these plots at $\lambda^2 = 0$ and the values of ratio of carrier concentration to effective mass are listed in Table 1 as a function of glass composition. The dependence of refractive index and dielectric constant on composition of glasses is rather nonlinear and is observed to be similar to other amorphous materials [12]. The values of refractive index, n_0 are calculated from optical dielectric constants ε^1 for all the wavelengths, λ^2. These values are found to be more or less same thoughout the wavelength range (350 to 800 nm). Therefore, average values of n_0 are reported in this wavelength region. The average value of refractive index n_0 shows dependence on PbO composition.

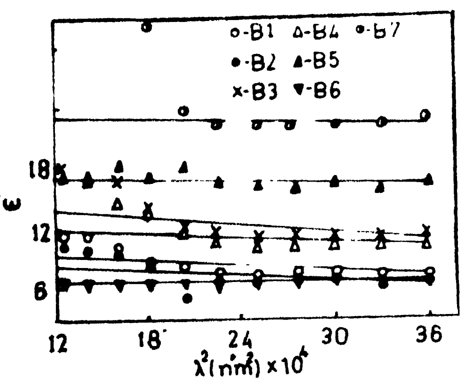

Figure 4. Dielectric constant *versus* λ^2.

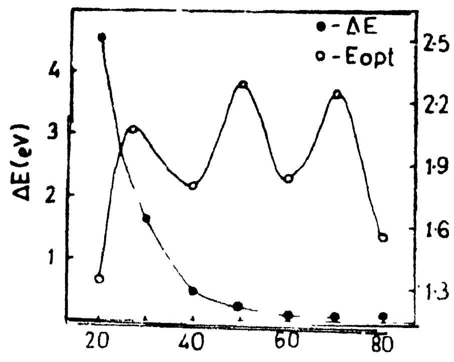

Figure 5. Optical energy gap E_{opt} and band tailing energy ΔE *versus* composition (PbO mol %)

The variation of ΔE, the width of the tail of localized states in the normally forbidden gap against PbO (mol %) is shown in Figure 5. The optical energy gap, E_{opt} is found to be minimum for the glass sample having 20 (mol %) of PbO and ΔE for 80 (mol %) of PbO. The decreasing trend of the band tailing energy suggests presence of sharp localized states in the band gap.

The ratio of carrier concentration to the effective mass, N/m^* has been calculated from the slope of the plot ε^1 *versus* λ^2 (Figure 4). The values of N/m^* for different glass samples are tabulated in Table 1. It has been observed that the values are found to be of the order of 10^{21} cm^{-3} which are in agreement with the values reported in oxide glasses [17] and calculated by other methods. The ratio N/m^* is found to be less for 70 (mol %) of PbO.

4. Conclusion

The optical gap (E_{opt}) is found to depend on concentration of PbO. The band tailing factor is found to decrease with increasing content of PbO. The refractive index (n_0) calculated in the region 350 to 800 nm is found to increase with increasing content of PbO except for the glass composition 30, 50 and 70 (mol %) of PbO. The optical energy gap is less for 20 (mol %) of PbO glass composition. The ratio of carrier concentration to the effective mass (N/m^*) is found to be of the order of 10^{21} (cm^{-3}). The straight line behaviour in Figure 3 suggests forbidden indirect transition.

Acknowledgment

Authors wish to thank Prof. V G Bhamburkar, Principal, Shri Shivaji Science College, Amravati for providing the necessary laboratory facilities during the progress of this work.

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